

# Magnetism and unconventional superconductivity in $\text{Ce}_n\text{M}_m\text{In}_{3n+2m}$ heavy-fermion crystals

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## Abstract

We review magnetic, superconducting and non-Fermi-liquid properties of the structurally layered heavy-fermion compounds  $\text{Ce}_n\text{M}_m\text{In}_{3n+2m}$  ( $\text{M}=\text{Co, Rh, Ir}$ ). These properties suggest d-wave superconductivity and proximity to an antiferromagnetic quantum-critical point.

*Key words:*  $\text{Ce}_n\text{M}_m\text{In}_{3n+2m}$ ; d-wave superconductivity; quantum criticality

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The report [1] of pressure-induced superconductivity in the heavy-fermion compound  $\text{CeRhIn}_5$ , with a transition temperature exceeding 2 K, has motivated further exploration [2,3,4,5] of this compound and the broader family of materials  $\text{Ce}_n\text{M}_m\text{In}_{3n+2m}$ , where M is a transition metal Co, Rh or Ir. Diffraction studies [6,7] show that the family can be considered a structural hybrid of  $\text{CeIn}_3$  and ' $\text{MIn}_2$ '; for  $n=1$ , single layers of  $\text{CeIn}_3$  and ' $\text{MIn}_2$ ' are stacked sequentially along the tetragonal c-axis, and for  $n=2$  there are two adjacent layers of  $\text{CeIn}_3$  separated by a single layer of ' $\text{MIn}_2$ '. Crystallographic layering in the  $n=1$  members produces electronic anisotropy, reflected particularly in a Fermi surface dominated by a slightly warped cylindrical sheet. [8,9,10,11] Though these materials should not be considered strictly 2-dimensional, their electronic and structural anisotropies do influence magnetic, superconducting and quantum-critical properties. In the following, we briefly review what has been learned about some of these properties.

The infinite-layer (cubic), parent of this family,  $\text{CeIn}_3$ , orders antiferromagnetically near 10 K at atmospheric pressure. Applying pressure suppresses its Néel temperature toward  $T=0$  at a critical pressure  $P_c \approx 2.6$  GPa, where a 'dome' of superconductivity appears in a narrow pressure window centered around  $P_c$ . [12] The single and bilayer members with  $\text{M}=\text{Rh}$  also order antiferromagnetically and become pressure-induced superconductors, but both with nearly an order of magnitude higher  $T_c$  [1,5] than the maximum of  $\sim 0.25$  K found in  $\text{CeIn}_3$ . Some magnetic prop-

	$T_N$ (K)	Q (h,k,l)	$\mu_o$ ( $\mu_B$ )	$P_c$ (GPa)
$\text{CeIn}_3$	10.2	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ [13,14]	0.65 [13]	$2.6 \pm 0.1$ [12]
			0.48 [14]	
$\text{CeRhIn}_5$	3.8 [1]	$(\frac{1}{2}, \frac{1}{2}, 0.297)$ [15]	0.37 [15]	$1.6 \pm 0.1$ [1]
$\text{Ce}_2\text{RhIn}_8$	2.8 [2]	$(\frac{1}{2}, \frac{1}{2}, 0)$ [16]	0.55 [16]	$3 \pm 0.5$ [5]
	1.65 [17]			$0.04 \pm 0.01$ [5]

Table 1

Magnetic properties of  $\text{Ce}_m\text{Rh}_n\text{In}_{3m+2n}$  and  $\text{CeIn}_3$ .  $T_N$ : Néel temperature; Q: antiferromagnetic propagation vector;  $\mu_o$ : ordered moment;  $P_c$ : critical pressure to suppress  $T_N$  to  $T=0$ .

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	$T_c$ (K)	$\Delta C/\gamma_n T_c$	$\gamma_n$ (J/mol K <sup>2</sup> )	$H_{c2}^{a,b}$ (T)	$H_{c2}^c$ (T)	$\partial H_{c2}^{a,b}/\partial T$ (T/K)	$\partial H_{c2}^c/\partial T$ (T/K)	$\xi_0^{a,b}$ (Å)	$\xi_0^c$ (Å)
CeIrIn <sub>5</sub>	0.4 [4]	0.76 [4]	0.70 [4]	1.0 [11]	0.49 [11]	-4.8 [4]	-2.54 [20]	260 [11]	180 [11]
CeCoIn <sub>5</sub>	2.3 [3]	4.5 [3]	0.35 [3]	11.9 [21] 11.6 [22]	4.95 [21,22]	-24.0 [22]	-8.2 [20] -11.0 [22]	82 [22]	53 [22]
CeRhIn <sub>5</sub> @ 2.1 GPa	2.12 [23]	0.36 [23]	0.38 [23]		10.2 [24] at 2.5 GPa		-15.0 [24] at 2.5 GPa	57 [24]	
Ce <sub>2</sub> RhIn <sub>8</sub> @ 1.63 GPa	1.1 [5]		$\approx 0.20$ [5]	5.4 [5]		-9.2 [5]			77 [5]

Table 2

Superconducting properties of  $\text{Ce}_m\text{T}_n\text{In}_{3m+2n}$ .  $T_c$ : superconducting transition temperature;  $\Delta C/\gamma_n T_c$ : jump in specific heat at  $T_c$  normalized by the Sommerfeld coefficient  $\gamma_n$  at  $T \geq T_c$ ;  $H_{c2}^{a,b}$  ( $H_{c2}^c$ ): upper critical field in the  $a$ - $b$  plane (parallel to the  $c$ -axis) extrapolated to  $T = 0$ ;  $\partial H_{c2}/\partial T$ : slope of the upper critical field near  $T_c$ ;  $\xi_0$ : Ginzburg-Landau superconducting coherence length at  $T = 0$ .

erties of these three compounds are summarized in table 1. The commensurate ordering  $Q$ -vector, ordered moment and  $P_c$  are similar in CeIn<sub>3</sub> and Ce<sub>2</sub>RhIn<sub>8</sub>; however, at 1.65 K, Ce<sub>2</sub>RhIn<sub>8</sub> also develops an incommensurate magnetic structure [17], as does CeRhIn<sub>5</sub>. From this comparison, the  $n = 2$  member superficially appears to be a magnetic hybrid of the  $n = 1$  and  $n = \infty$  members, as might be expected from its crystal structure. Inelastic neutron scattering studies [18] of CeRhIn<sub>5</sub> find that magnetic correlations develop on a temperature scale roughly twice  $T_N$ . The correlation length along the tetragonal  $c$ -axis  $\xi_c \approx 1.3$   $\text{c}$ ; whereas, in the  $\mathbf{a}$ - $\mathbf{b}$  plane, the correlation length  $\xi_a \approx 5$   $\text{a}$ , reflecting magnetic anisotropy that may be important for superconductivity. Presently, we do not know if this anisotropy changes as the antiferromagnetic-superconducting boundary is approached with applied pressure, but it appears [19] that the  $c$ -axis discommensuration  $\delta$  is somewhat pressure dependent.

A rather remarkable characteristic of this family of materials is their instability to superconductivity. Besides CeIn<sub>3</sub>, CeRhIn<sub>5</sub> and Ce<sub>2</sub>RhIn<sub>8</sub> under pressure, CeIrIn<sub>5</sub> and CeCoIn<sub>5</sub> are superconducting at atmospheric pressure. See table 2. In each case, superconductivity develops out of a highly correlated state with a large specific heat Sommerfeld coefficient  $\gamma_n$  and in proximity to antiferromagnetism. For example, substituting a small amount of Rh into CeCo<sub>1-x</sub>Rh<sub>x</sub>In<sub>5</sub> or CeIr<sub>1-x</sub>Rh<sub>x</sub>In<sub>5</sub> induces antiferromagnetism, and, for a range of  $x$  (roughly  $0.3 \lesssim x \lesssim 0.7$ ), homogeneous coexistence of superconductivity and antiferromagnetism. [25,26,27] The superconducting transition temperatures also are high compared to other heavy-fermion examples. With applied pressure, all compounds listed in table 2 have  $T_c$ s between 2.2 and 2.6 K [5,24,28], except CeIrIn<sub>5</sub> whose bulk  $T_c$  reaches  $\approx 1$  K at 2.1 GPa [29,30] and does not exceed 1.2 K at pressures to 4 GPa [31].

Electronic anisotropy is reflected in an upper criti-

cal magnetic field that is typically two times larger for  $H \parallel \mathbf{a} - \mathbf{b}$  plane than for  $H \parallel c$ -axis. In many cases, the measured  $H_{c2}(0)$  exceeds the Pauli paramagnetic limit  $H_P/T_c = 1.86$  T/K. [32] In this regard, CeCoIn<sub>5</sub> has been studied most extensively and, for  $H \parallel [001]$ , exhibits a first order phase transition in a narrow field range at low temperatures [33], which is attributed to Pauli limiting. For  $H \parallel [110]$ , a magnetically hysteretic transition develops below  $0.6T_c$  that is consistent with the formation of a spatially inhomogeneous Fulde-Ferrel-Larkin-Ovchinnikov state. [21] This possibility deserves further study. Additionally,  $H_{c2}(0)$  is weakly, but clearly, anisotropic within the basal plane [21,34], implying the possibility of non-s-wave pairing.

There is growing evidence, summarized in table 3, that superconductivity in members of the family is unconventional. Power laws found deep in the superconducting state,  $C/T \propto T$ , thermal conductivity  $\kappa \propto T^3$  and spin-lattice relaxation rate  $1/T_1 \propto T^3$ , are those expected of an order parameter with line nodes. Together with Knight shift measurements [36,42] on CeCoIn<sub>5</sub>, these power laws suggest unconventional spin-singlet superconductivity, and, indeed, thermal conductivity measurements [34] find a prominent four-fold modulation in  $\kappa$  as a magnetic field is rotated in

	$C/T$	$\kappa$	$1/T_1$	$\lambda$
CeIrIn <sub>5</sub>	$T$ [20]	$T^3$ [20]	$T^3$ [35,36]	$T^{1.5 \pm 0.2}$ [37]
CeCoIn <sub>5</sub>	$T$ [20]	$T^{3.37}$ [20]	$T^{3+\varepsilon}$ [36]	$T^{1.65 \pm 0.2}$ [37] $T^{1+\varepsilon}$ [38] $T^{1.5}$ [39] $T^{\frac{3}{2}}/T$ [40]
CeRhIn <sub>5</sub> @ 2.1 GPa	$T$ [23]		$T^3$ [41]	

Table 3

Power laws in the superconducting state.  $C/T$ : specific heat divided by temperature;  $\kappa$ : electronic thermal conductivity;  $1/T_1$ : spin-lattice relaxation rate;  $\lambda$ : superconducting penetration depth.

	$C/T$	$\rho$	$1/T_1 T$
$\text{CeIn}_3$		$T^{1.5-1.6}$ [12] near $P_c$	const. [43] $P \geq P_c$
$\text{CeIrIn}_5$	$\gamma_0 - AT^{\frac{1}{2}}$ [44] for $H = 6$ T	$T^{1.3}$ [4]	$(T+8)^{-\frac{3}{4}}$ [35] $(T+0.86)^{-\frac{1}{2}}$ [36]
$\text{CeCoIn}_5$	$-\ln T$ [3,45]	$T^{1.0 \pm 0.1}$ [28,45]	$\sim T^{-\frac{3}{4}}$ [36]
$\text{CeRhIn}_5$		$T^1$ [24] $P = 3.2$ GPa	$(T+1.5)^{-\frac{1}{2}}$ [41] $P = 2.1$ GPa
$\text{Ce}_2\text{RhIn}_8$		$T^{0.95 \pm 0.05}$ [5] $P = 1.63$ GPa	

Table 4

Non-Fermi-liquid behaviors.  $C/T$ : specific heat divided by temperature;  $\rho$ : electrical resistivity in the  $a - b$  plane;  $1/T_1 T$ : spin-lattice relaxation rate divided by temperature.

the basal plane. The magnitude and location of maxima in  $\kappa(\theta)$  are consistent with an order parameter having  $d_{x^2-y^2}$  symmetry.

The boson mediating Cooper pairing remains unknown, but the preponderance of evidence points to antiferromagnetic spin fluctuations. The temperature dependence of some normal state properties further suggests that these fluctuations may not be conventional. For a Landau Fermi liquid,  $C/T \sim \text{constant}$ ,  $\rho \sim T^2$ , and  $1/T_1 T \sim \text{constant}$  are expected at low temperatures. As shown in table 4, this is not the case for several family members. These distinctly non-Fermi-liquid behaviors are expected [46] near an antiferromagnetic quantum-critical point and are found for the examples in table 4 only in  $T - P - H$  space close to superconductivity. The functional dependencies, particularly  $\rho \propto T$ , suggest 2-dimensional antiferromagnetic quantum fluctuations. Understanding the interplay of electronic and magnetic anisotropies with quantum-critical fluctuations and superconductivity is one problem posed by this interesting family of heavy-fermion compounds.

Finally, we note the possible existence of a spin pseudogap in  $\text{CeRhIn}_5$  near its critical pressure  $P_c$  [43] and in  $\text{CeCoIn}_5$  for  $0 \leq P \lesssim 1.6$  GPa [28]. The small difference in temperature scale ( $\sim 5$  K and  $\sim 3$  K, respectively) on which a pseudogap signature appears in these two compounds seems to be related to their relative cell volumes. [28] An analysis of systematic changes in thermodynamic and transport properties of  $\text{Ce}_{1-x}\text{La}_x\text{CoIn}_5$  further suggests a connection between the possible pseudogap in  $\text{CeCoIn}_5$  and the development of short-range antiferromagnetic correlations. [45]

Acknowledgements Work at Los Alamos was performed under the auspices of the U.S. DOE Office of

Science. ZF acknowledges support by NSF grant DMR-9971348. We also thank V. A. Sidorov and H. A. Borges for communicating results of their unpublished pressure measurements.

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